

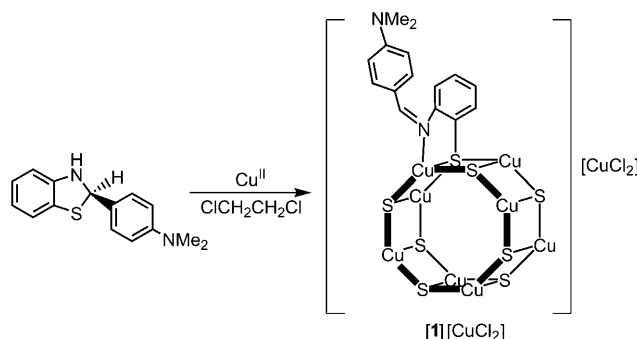
# Reversible Conversion of Electronic Structures in a Cyclic Octacopper Complex

Tatsuya Kawamoto,<sup>\*,[a, c]</sup> Masato Nishiwaki,<sup>[a]</sup> Makiko Nishijima,<sup>[a]</sup> Koichi Nozaki,<sup>[b]</sup> Asako Igashira-Kamiyama,<sup>[a]</sup> and Takumi Konno<sup>[a]</sup>

Redox-active molecular systems have received great attention not only in the field of fundamental chemistry, but also in many fields of application. In coordination chemistry, a number of redox-active transition metal complexes have been synthesized by using the non-innocent character of ligands, and their electronic structures as well as their optical and magnetic properties have been extensively investigated.<sup>[1]</sup> For example, it has been reported that square-planar metal complexes with non-innocent semiquinonate-type ligands show rich electrochemical behavior, which has been attributed to ligand-centered redox processes.<sup>[2]</sup> The construction of dimensional structures by using redox-active metal complexes as building blocks has also been carried out for the continuing development of functional materials.<sup>[3]</sup> Conversely, reports on discrete redox-active complexes, not metal-centered redox, with a high nuclearity are limited in number, and much less is known about the electronic structures and properties of these species.<sup>[4]</sup> Herein, we report a cyclic sulfur-bridged octacopper complex that undergoes a clear interconversion between its neutral, monocationic, and dicationic species. Notably, the monocationic and dicationic species exhibit characteristic, intense ab-

sorption in the near-infrared (NIR) region, which is an important property for applications involving telecommunications and optical data storage.<sup>[4,5]</sup> To the best of our knowledge, this is the first example of a non-innocent polynuclear system, the character of which comes from S-bridged metal-core structure rather than organic ligands.

The reaction of 2-(4-dimethylaminophenyl)benzothiazoline with copper(II) acetate monohydrate in a 2:1 ratio in 1,2-dichloroethane under a nitrogen atmosphere gave an almost black solution from which a dark brown powder ([1]-[CuCl<sub>2</sub>]) was isolated by adding diethyl ether (Scheme 1).



Scheme 1. Synthesis of [1][CuCl<sub>2</sub>]. Only one of eight ((4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)C(H)=NC<sub>6</sub>H<sub>4</sub>) moieties is presented for clarity.

The presence of a disulfide organic compound (2,2'-di(4-dimethylaminophenyl)methyleneaminophenyl)disulfide in the filtrate implies that 2-(4-dimethylaminophenyl)benzothiazoline acts not only as a ligand but also as a reducing agent for copper(II).<sup>[6]</sup> The lack of the  $\tilde{\nu}_{\text{N-H}}$  vibration in the IR spectrum of this compound is in accordance with the coordination of the ligand in an iminothiolate-N,S mode.

The structure of [1][CuCl<sub>2</sub>] was determined by single-crystal X-ray analysis, which revealed the presence of discrete complex cations and linear anions, [1]<sup>+</sup> and [Cu<sup>I</sup>Cl<sub>2</sub>]<sup>-</sup>, respectively. The 1:1 ratio of cations and anions in the unit

[a] Dr. T. Kawamoto, M. Nishiwaki, M. Nishijima, Dr. A. Igashira-Kamiyama, Prof. T. Konno  
Department of Chemistry  
Graduate School of Science  
Osaka University, Toyonaka, Osaka 560-0043 (Japan)

[b] Prof. K. Nozaki  
Department of Chemistry  
Graduate School of Science and Engineering  
University of Toyama, Toyama, Toyama 930-8555 (Japan)

[c] Dr. T. Kawamoto  
Current address: Department of Chemistry  
Faculty of Science  
Kanagawa University, Hiratsuka, Kanagawa 259-1293 (Japan)  
Fax: (+81) 463-58-9684  
E-mail: kaw@kanagawa-u.ac.jp

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200801614>.

cell implies that the complex cation is in a monocationic form. As shown in Figure 1, the entire complex  $[1]^+$  contains eight Cu atoms that are bridged by eight iminothiolate

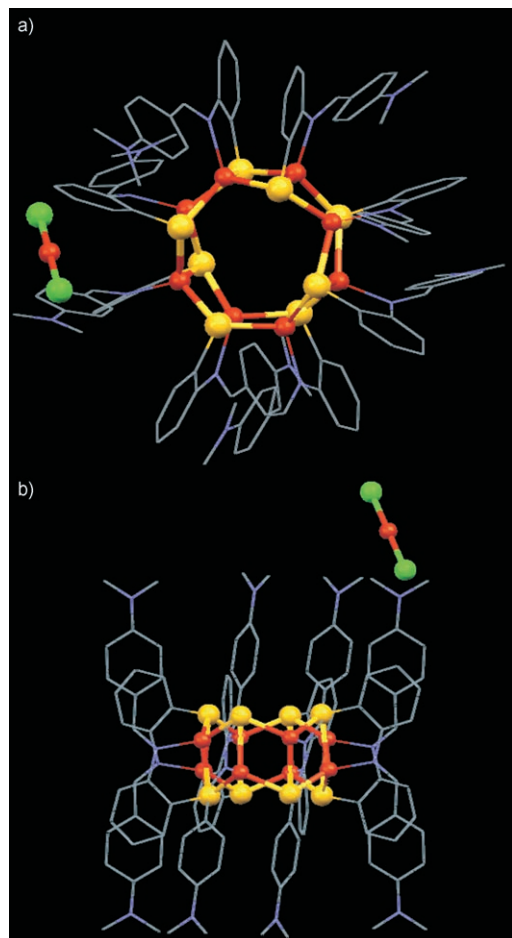


Figure 1. a) Top view and b) side view of  $[1][CuCl_2]$ ; copper, red; sulfur, yellow; nitrogen, blue; chlorine, green; carbon, gray.

ligands ( $L=S(C_6H_4)N=CH(C_6H_4NMe_2)$ ) through the S atoms to construct a cyclic-ladder structure with a  $Cu_8S_8$  octagonal prism. Given that each Cu atom is in a +1 oxidation state and each iminothiolate ligand is monoanionic, this octacopper complex should be neutral. Thus, one electron is removed from the entire octanuclear structure to form the monocationic  $[1]^+$ . Each copper atom in  $[1]^+$  is tetrahedrally coordinated by N and S atoms from one chelating ligand and two  $\mu_3$ -S atoms from two neighboring ligands. The Cu...Cu distances (2.569(2)–2.671(2) Å) in  $[1]^+$  are appreciably shorter than the sum of van der Waals radii of 2.82 Å,<sup>[7]</sup> suggestive of the presence of metal–metal interactions (Figure S1 in the Supporting Information).<sup>[8]</sup> These distances are much shorter than those found in related copper(I) thiolate complexes.<sup>[9]</sup>

The electronic absorption spectrum of  $[1][CuCl_2]$  in 1,2-dichloroethane is characterized by a broad, intense band at  $\lambda=1770$  nm ( $\epsilon=2.56 \times 10^4$  M<sup>−1</sup> cm<sup>−1</sup>). On standing the solu-

tion of  $[1][CuCl_2]$  in 1,2-dichloroethane under aerobic condition, the band at  $\lambda=1770$  nm slowly decreased with the appearance and increase of a relatively sharp, intense band at  $\lambda=1220$  nm ( $\epsilon=8.45 \times 10^4$  M<sup>−1</sup> cm<sup>−1</sup>). This absorption spectral change with time of  $[1][CuCl_2]$  was accelerated in polar solvents such as methanol and ethanol, and thus a brown compound ( $[1][ClO_4]$  or  $[1][PF_6]$ ) that shows an intense band at  $\lambda=1220$  nm was isolated from a methanol solution of  $[1][CuCl_2]$  by adding NaClO<sub>4</sub> or NH<sub>4</sub>PF<sub>6</sub>.<sup>[10]</sup> Single-crystal X-ray analysis of  $[1][PF_6]$  indicated the presence of two PF<sub>6</sub><sup>−</sup> ions per one complex cation, implying that the entire complex cation ( $[1]^{2+}$ ) is dicationic (Figure S2 in the Supporting Information). The overall structure of  $[1]^{2+}$  is essentially the same as that of  $[1]^+$  and has a cyclic ladder structure with a  $Cu_8S_8$  octagonal-prism core composed of eight Cu atoms and eight iminothiolate ligands.

The cyclic voltammogram (CV) of  $[1][CuCl_2]$  was recorded in 1,2-dichloroethane containing 0.1 M [Bu<sub>4</sub>N]BF<sub>4</sub>, as a supporting electrolyte, at a glassy carbon working electrode and an Ag/Ag<sup>+</sup> reference electrode. The CV exhibits two almost reversible redox waves at  $E_{1/2}^1=-0.36$  V and  $E_{1/2}^2=-0.77$  V (Figure 2). The spectroelectrochemical experiments

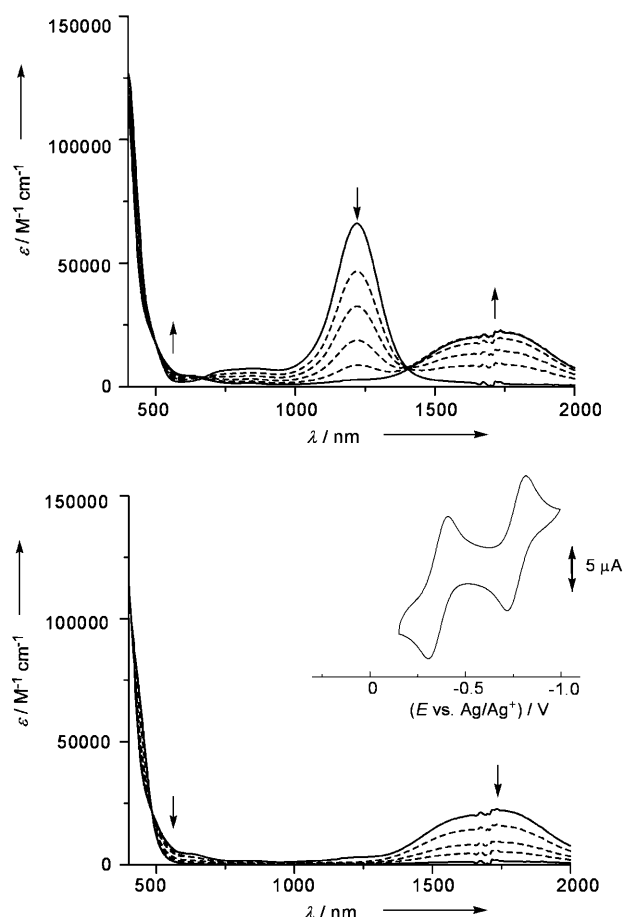
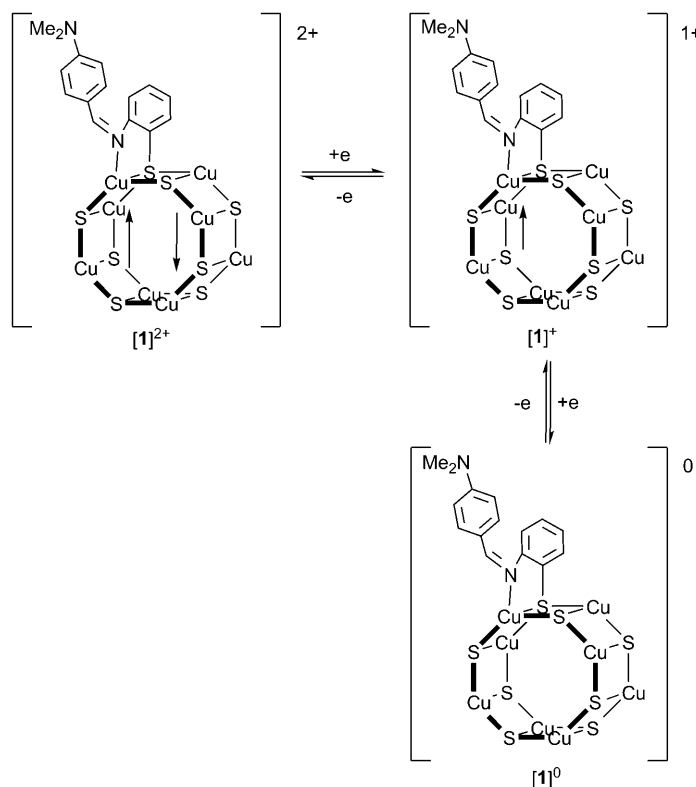


Figure 2. UV/Vis/NIR spectral changes for two successive electrochemical reductions from −0.2 V to −0.6 V (top) and from −0.6 V to −1.0 V (bottom) for  $[1][CuCl_2]$  in ClCH<sub>2</sub>CH<sub>2</sub>Cl. The inset shows a cyclic voltammogram of  $[1][CuCl_2]$  with a scan rate of 0.1 V s<sup>−1</sup>.

were also carried out using an optically transparent thin layer electrode (OTTLE) cell in 1,2-dichloroethane (Figure 2). At  $-0.2$  V, the absorption spectrum is the same as that of  $[1]^{2+}$ , and has a characteristic intense band at  $\lambda = 1220$  nm, indicative of the existence of the dicationic species at this potential. If the potential was decreased from  $-0.2$  V, the band at  $\lambda = 1220$  nm gradually decreased with the appearance of a broad band at  $\lambda = 1770$  nm, and the spectrum recorded at  $-0.6$  V was identical to that of  $[1]^+$ . Several isosbestic points were maintained during the spectral change. These results clearly indicate that  $[1]^{2+}$  and  $[1]^+$  are electrochemically interconvertible to each other, retaining the cyclic octacopper structure. If the potentials were changed from  $-0.6$  V to  $-1.0$  V, the broad band at  $\lambda = 1770$  nm decreased and finally no absorption band was observed in the NIR region at  $-1.0$  V. The existence of several isosbestic points establishes the quantitative interconversion between  $[1]^+$  and its one-electron reduction species,  $[1]^0$ . From these results, it is reasonable to assume that  $[1]^0$  also has the same S-bridged cyclic octacopper structure as those found in  $[1]^{2+}$  and  $[1]^+$ , although attempts to isolate  $[1]^0$  were unsuccessful. The absorption spectral behavior of an isolated neutral species ( $[1a]^0$ ) that matches well with that of  $[1]^0$ , was achieved by using benzothiazoline with trifluoromethyl group instead of dimethylamino group (Figure S3 in the Supporting Information), and its cyclic octacopper structure was unambiguously confirmed by single-crystal X-ray analysis. As in the case of  $[1]^+$ , the CV of  $[1a]^0$  in 1,2-dichloroethane displayed two reversible redox waves. However, their potentials ( $E_{1/2}^1 = 0.09$  V and  $E_{1/2}^2 = -0.28$  V) are greatly positively shifted compared with those for  $[1]^+$ , which led to the isolation of  $[1a]^0$ .

To get insight into the electronic states of complexes, the density functional theory (DFT) calculations using Gaussian 03 program suite<sup>[11]</sup> were performed for the model compounds ( $[1b]^{2+}$ ,  $[1b]^+$ , and  $[1b]^0$ ) of the  $Cu_8S_8$  species in which dimethylamino groups are replaced by hydrogens (Figure S4–S6 in the Supporting Information). The DFT calculations showed that the neutral species ( $[1b]^0$ ) is singlet ( $S=0$ ) and the HOMO (MO-320) is occupied by a couple of electrons. The dicationic species ( $[1b]^{2+}$ ) is also singlet, but the  $\alpha$ -spin and  $\beta$ -spin electrons reside without complete pairing in the lowest energy state; the occupied MO-317 for  $\alpha$ -spin is vacant for  $\beta$ -spin (MO-320), whereas the occupied MO-317 for  $\beta$ -spin is unoccupied for  $\alpha$ -spin (MO-320).<sup>[12]</sup> On the other hand, the monocationic species ( $[1b]^+$ ) is doublet ( $S=1/2$ ), and its Mulliken spin densities show the presence of 88% spins on the  $Cu_8S_8$  core: Cu, 0.328 (0.0351–0.0451 for Cu atoms); S, 0.554 (0.0607–0.0860 for S atoms). The ESR spectrum in the solid state of  $[1][CuCl_2]$  at 77 K exhibited an isotropic signal centered at  $g=2.05$  (peak-to-peak line width of 12.5 G) without a Cu hyperfine coupling. These findings indicate that the odd electron in  $[1]^+$  is not localized on the metal centers to form a mixed-valence  $Cu^I Cu^II$  state, but is distributed around the entire  $Cu_8S_8$  core to give a non-innocent state. Absorption spectra in the Vis-NIR region were also calculated for  $[1b]^{2+}$ ,  $[1b]^+$ , and  $[1b]^0$  by using time-dependent DFT calculation. The absorp-

tion spectra of  $[1b]^+$  and  $[1b]^{2+}$ , which were simulated based on the calculated excitation energies and oscillator strengths for 50 excitations (Figure S8 in the Supporting Information),<sup>[13]</sup> reproduce fairly well the features of the observed spectra of  $[1]^+$  and  $[1]^{2+}$ , respectively (Figure S9 in the Supporting Information). In addition, the simulated spectrum of  $[1b]^0$  is also in good agreement with the spectrum of  $[1]^0$  observed in the spectroelectrochemistry and exhibits no absorption band in the NIR region. The calculations for  $[1b]^+$  and  $[1b]^{2+}$  indicated that the NIR absorption bands are assigned to the intra  $Cu_8S_8$  core transitions, i.e., MO-312→MO-320 and MO-314→MO-320, owing to singlet diradicals ( $S=0$ ) for  $[1b]^{2+}$  and MO-317→MO-320, MO-318→MO-320, and MO-319→MO-320, owing to a doublet monoradical ( $S=1/2$ ) for  $[1b]^+$  (Table S1 in the Supporting Information). Thus, the time-dependent DFT calculations provided a reasonable MO interpretation of the experimental electronic absorption spectra and a summary of all elucidated electronic structures of octanuclear species is illustrated in Scheme 2.



Scheme 2.

In conclusion, from the reaction of 2-substituted benzothiazoline with copper(II), we created a new type of redox-active coordination system, in which dicationic ( $[1]^{2+}$ ), monocationic ( $[1]^+$ ), and neutral ( $[1]^0$ ) species are interconvertible to one another with retention of the cyclic  $Cu_8S_8$  core structure. The dicationic and monocationic species possess radicals that are delocalized over the  $Cu_8S_8$  core and

show a characteristic intense absorption band in the NIR region. Remarkably, this system displayed a drastic change in NIR absorptions by changing the oxidation states among  $[1]^{2+}$ ,  $[1]^+$ , and  $[1]^0$ . Current efforts are focusing on the control of redox potentials and NIR absorption energies of this class of non-innocent complexes by means of the modification of substituent groups on benzothiazolines.

## Experimental Section

Experimental details, together with spectroscopic data, are given in the Supporting Information.

## Acknowledgements

The authors thank Dr. K. Yamaguchi and Prof. S. Suzuki for ESR measurement.

**Keywords:** copper • density functional calculations • diradicals • electronic structure • sulfur

- [1] E. I. Stiefel, *Prog. Inorg. Chem.* **2004**, 52. This book is devoted to dithiolene chemistry.
- [2] a) P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, 123, 2213; b) D. Herebian, E. Bothe, E. Bill, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, 123, 10012; c) P. Ghosh, A. Begum, D. Herebian, E. Bothe, K. Hildenbrand, T. Weyhermüller, K. Wieghardt, *Angew. Chem.* **2003**, 115, 581; *Angew. Chem. Int. Ed.* **2003**, 42, 563; d) K. Ray, T. Weyhermüller, F. Neese, K. Wieghardt, *Inorg. Chem.* **2005**, 44, 5345.
- [3] N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, 227, 93.
- [4] a) M. D. Ward, J. A. McCleverty, *J. Chem. Soc. Dalton Trans.* **2002**, 275; b) M. D. Ward, *J. Solid State Electrochem.* **2005**, 9, 778.
- [5] a) J. Fabian, H. Nakazumi, M. Matsuoka, *Chem. Rev.* **1992**, 92, 1197; b) R. J. Mortimer, N. M. Rowley, *Comprehensive Coord. Chem. II*, **2003**, 9, 581.
- [6] T. Kawamoto, N. Ohkoshi, I. Nagasawa, H. Kuma, Y. Kushi, *Chem. Lett.* **1997**, 553. The formation of disulfides was confirmed in comparison with an authentic sample, which was independently prepared.
- [7] A. Bondi, *J. Phys. Chem.* **1964**, 68, 441.
- [8] C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips, K.-H. Leung, *Angew. Chem.* **2000**, 112, 4250; *Angew. Chem. Int. Ed.* **2000**, 39, 4084.
- [9] a) D. M. Knötter, H. L. van Maanen, D. M. Grove, A. L. Spek, G. van Koten, *Inorg. Chem.* **1991**, 30, 3309; b) M. D. Janssen, J. G. Donkersvoort, S. B. van Berlekom, A. L. Spek, D. M. Grove, G. van Koten, *Inorg. Chem.* **1996**, 35, 4752.
- [10] The absorption band at  $\lambda = 1220$  nm for  $[1](\text{ClO}_4 \text{ or } \text{PF}_6)_2$  is reminiscent of the charge transfer band observed for neutral square-planar  $d^8$  complexes with non-innocent ligands (see Ref. [2]) or organic mixed-valence compounds, and the absorption band at  $\lambda \approx 1770$  nm for  $[1][\text{CuCl}_2]$  resembles the charge transfer band observed for their one-electron-reduced species; a) S. V. Lindeman, S. V. Rosokha, D. Sun, J. K. Kochi, *J. Am. Chem. Soc.* **2002**, 124, 843; b) P. J. Low, M. A. J. Paterson, H. Puschmann, A. E. Goeta, J. A. K. Howard, C. Lambert, J. C. Cherryman, D. R. Tackley, S. Leeming, B. Brown, *Chem. Eur. J.* **2004**, 10, 83; c) S. Barlow, C. Risko, S.-J. Chung, N. M. Tucker, V. Coropceanu, S. C. Jones, Z. Levi, J.-L. Brédas, S. R. Marder, *J. Am. Chem. Soc.* **2005**, 127, 16900.
- [11] Gaussian 03, Revision D.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Ciołowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [12] Compound  $[1][(\text{ClO}_4)_2]$  was essentially EPR silent. Consistent with this, sharp resonances were observed in the  $^1\text{H}$  NMR spectra of  $[1]^{2+}$  in  $[\text{D}_4]1,2$ -dichloroethane (Figure S7). These results imply that two spins in  $[1]^{2+}$  are antiferromagnetically coupled to yield an  $S=0$  ground state.
- [13] The broadening of the observed absorption bands were simulated with convolution of Gaussian line shape function having a full width at half maximum of  $\bar{\nu} = 1800 \text{ cm}^{-1}$ .

Received: August 5, 2008  
Published online: September 26, 2008